Isotopic equilibrium in a hydrogen plus alkali-metal hydroxide system

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The equilibrium isotope separation coefficient for hydrogen and potassium or sodium hydroxide crystals is measured. It is shown that a significant contribution to the separation effect is made not only by atomic oscillations in the hydrogen molecule or hydroxide ion, but also by oscillations due to interion interaction in the crystals.

The statistical theory of thermodynamic isotope effects allows us to calculate very accurately the magnitude and temperature dependence of the equilibrium isotope separation coefficient for systems composed of ideal gases. The presence of a condensed phase in a system makes it difficult to carry out such calculations since it is necessary to allow for the intermolecular and interionic interactions in the crystal or liquid in question. Therefore, it is necessary to use semiempirical relationships.[1] Since the energy spectra of the simplest crystals can be determined completely, it is possible to calculate the isotope separation coefficient for a system composed of lithium hydride and hydrogen with deuterium impurities[2] and to obtain good agreement with the experimental data.[3]

In order to refine and develop the ideas on the role of the isotopic defects in crystals, it would be very useful to extend the range of materials investigated experimentally. We shall consider crystals of alkali hydroxides because the isotopic effect is greatest for hydrogen. Moreover, a proton is a component of a hydroxyl ion and this is the simplest asymmetric ion that can be used to study crystals of noncubic symmetry.

1. MEASUREMENT OF THE EQUILIBRIUM DISTRIBUTION OF ISOTOPES BETWEEN CRYSTALS AND HYDROGEN

Many aspects of our experiments were similar to those described in[3]. Hydrogen used in the isotope-exchange experiments was generated in a laboratory electrolytic unit. The traces of oxygen were removed in a palladium catalyst and the hydrogen was dried in a liquid-nitrogen trap. Potassium and sodium hydroxides of the "chemically pure" grade were heated above the melting point and dehydrated by pumping for several hours in 10^{-2} torr vacuum. The hydroxide crystals were then ground in a dry chamber and sifted by a system of sieves. The isotopic composition was determined by passing hydrogen through heated cupric oxide. Water formed by vacuum distillation was used in a flotation analysis.[4] The isotopic composition of the crystals was determined using a float in water which was obtained by the reaction

$$\mathrm{MeOH} + \mathrm{CO_2} \rightarrow \mathrm{Me_2CO_3} + \mathrm{H_2O}.$$

The isotopic equilibrium was confirmed by comparing the results of experiments carried out using samples with different isotopic compositions of the two phases and by verifying that the results were reproducible.

TABLE I. Experimental results and conditions

Grain size, mm	Initial conditions*	Contact time, h	T, °C	Equilibrium isotopic composition, at.% D		α
				Crystals	Gas	
			KOH·NaOH			
0.13—0.26	$x_0 < y_0$	170	150	2,79	1,53	1.84
0.13—0.26	$x_0 < y_0$	120	150	2.21	1.20	1.86
0.13—0.26	$x_0 > y_0$	170	125	1.74	0.88	2.00
0.05—0.13	$x_0 < y_0$	170	125	2.37	1.16	2.06
< 0.05	$x_0 > y_0$	125	125	2.72	1.36	2.02
0.05—0.13	$x_0 < y_0$	145	125	1.74	0.85	2.07
< 0.05	$x_0 > y_0$	1500	100	1.81	0.79	2.31
< 0.05	$x_0 > y_0$	1000	94	1.44	0.60	2.44
< 0.05	$x_0 < y_0$	1000	94	1.46	0.62	2,39
			KOH			
0,26—0,80	$x_0 > y_0$	400	250	2.56	1.63	1.57
0,26—0,80	$x_0 < y_0$	400	200	3.18	1.84	1.75
0,26—0,80	$x_0 < y_0$	400	200	3.37	2.01	1.70
0,13—0,26	$x_0 > y_0$	1000	150	3.07	1.58	1.97
0,13—0,26	$x_0 > y_0$	1000	100	3.25	1.36	2.30
0,13—0,26	$x_0 > y_0$	1000	100	3.16	1.40	2.29

*Here, x_0 and y_0 represent the isotopic composition of the crystals and gas at the beginning of an experiment.

The experiments were carried out on KOH crystals below the polymorphic transition temperature (250° C) and on KOH·NaOH crystals (of eutectic composition). Table I lists all the experimental data which we obtained. The relative error was not more than 5%. This error was mainly due to the errors in the determination of the isotopic compositions of the phases. In both systems deuterium concentrated preferentially in the crystals. An analysis of the results in Table I by the least-squares method demonstrated that the values of the isotope separation coefficient for the KOH-hydrogen system were

$$\alpha_{\mathrm{KOH}} = (0.593 \pm 0.02) \exp (502 \pm 30) / T, \qquad (1)$$

whereas for the system KOH·NaOH-hydrogen the results obtained in the 94–150°C range were

$$\alpha_{\mathrm{eut}} = (0.332 \pm 0.04) \exp (720 \pm 50) / T, \qquad (2)$$

where T is the absolute temperature and the quoted errors represent the standard deviations.[5]

2. DISCUSSION OF RESULTS

It is evident from Eqs. (1) and (2) that the temperature dependence of the isotope separation coefficient is weaker for the KOH-hydrogen system than for the system with eutectic crystals. Since both these systems contain the same gaseous phase (hydrogen), it is natural to assume that the experimentally observed differences in the isotope separation coefficient are due to the crystalline phase. The contribution of this phase to the separation coefficient can be found by using

$$\beta_{\mathrm{cr}} = \alpha\beta_{\mathrm{g}}, \qquad (3)$$

where β_{cr} and β_{g} are the β factors of the crystal and gas (these factors represent the thermodynamic inequivalence of the hydrogen isotopes in a crystal and in a gas[6]). In the range of temperatures of interest to us, it follows from the treatment in[6,7] that

$$\beta_{\mathrm{g}} = 0.873 \exp \{408.6 / T\}. \qquad (4)$$

It is clear from Eqs. (1)–(4) that

$$\beta_{\mathrm{KOH}} = (0.517 \pm 0.016) \exp \{(910 \pm 30) / T\}, \qquad (5)$$

$$\beta_{\mathrm{eut}} = (0.289 \pm 0.024) \exp \{(1140 \pm 50) / T\}. \qquad (6)$$

Since the quantities given above differ considerably from unity, it follows that the thermodynamic inequivalence of the hydrogen isotopes in potassium and sodium hydroxide crystals is considerable.

The values of the β factors obtained for crystals should be compared with the β factor of the hydroxyl ion OH^- on the assumption that this ion can rotate freely at a lattice site. According to the infrared spectrometry results, the valence-vibrational frequency varies little on transition from a free hydroxyl ion to a corresponding ion in a crystal (Table II).[7-10] This makes it possible to calculate the corresponding partition functions from the formulas for ideal gases. In the 300—1000°K we have

$$\beta_{OH} = 0.727 \exp\{726/T\}. \tag{7}$$

It follows from Eqs. (5)—(7) that the experimental values of the β factors of the crystals and of the hydroxyl ion are different and this is particularly true of the temperature dependence. Consequently, the thermodynamic inequivalence of the hydrogen isotopes in these crystals cannot be entirely due to the valence vibrations of the hydroxyl ion.

The ratio $\beta_{cr}/\beta_{OH} = \beta_{lat}$ can be called the lattice β factor, which is understood to be the contribution of the interionic interaction to the thermodynamic inequivalence of the isotopes in a crystal. According to the experimental results (Table III), the value of β_{lat} tends to unity as the temperature approaches a phase transition point. In the case of eutectic crystals, this happens near the melting point of 172°C, whereas in the case of KOH crystals the same occurs near the polymorphic transition temperature. We can explain these observations by considering a phase transition as the destruction of bonds in a given structure, including those responsible for the isotope separation effect. In the case of KOH crystals, these may be the hydrogen bonds between neighboring hydroxyl ions, whose presence is demonstrated in[10].

Thus, the isotope separation coefficient of systems formed by hydrogen and potassium and sodium hydroxide crystals is structure-sensitive. Its value is governed by quantum effects in the gaseous phase, the valence vibrations in the hydroxyl ion, and the interionic interaction in the crystal lattice.

TABLE II. Observed frequencies of O—H valence vibrations

Compound	T, °C	ω, cm^{-1}	Reference	Compound	T, °C	ω, см$^{-1}$	Reference
LiOH	20	3678	[8]	KOH	23	3600	[10]
NaOH	20	3637	[9]	free OH	—	3570	[7]

TABLE III. Values of β_{lat}

Crystal	T, °C	β_{lat}	Error	Crystal	T, °C	β_{lat}	Error
KOH	100	1.17	0.04	KOH·NaOH	100	1.20	0.06
KOH	150	1.10	0.04	KOH·NaOH	125	1.12	0.06
KOH	200	1.06	0.04	KOH·NaOH	150	1.06	0.06
KOH	250	1.00	0.04	KOH·NaOH	170	1.00	0.06

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[1] D. N. Knyazev, G. D. Klinskiĭ, and I. N. Rozhenko, Tr. Mosk. Khim.-Tekhnol. Inst. No. 67, 113 (1970).

[2] G. Benedek, R. F. Wallis, I. P. Ipatova, A. A. Klochikhin, and A. A. Maradudin, Fiz. Tverd. Tela **11**, 382 (1969) [Sov. Phys.-Solid State **11**, 303 (1969)].

[3] G. Ya. Ryskin and Yu. P. Stepanov, Zh. Eksp. Teor. Fiz. **56**, 541 (1969) [Sov. Phys.-JETP **29**, 299 (1969)].

[4] A. I. Shatenshtein, Izotopnyĭ analiz vody (Isotopic Analysis of Water), Izd. AN SSSR, M., 1957.

[5] V. V. Nalimov, Primenenie matematicheskoĭ statistiki pri analize veshchestva (Application of Mathematical Statistics to Analysis of Matter), Fizmatgiz, M., 1960.

[6] Ya. M. Varshavskiĭ and S. É. Vaĭsberg, Usp. Khim. **26**, 1434 (1957).

[7] V. P. Glushko (ed.), Termodinamicheskie svoĭstva individual'nykh veshchestv-spravochnik (Handbook on Thermodynamic Properties of Individual Substances), Izd. AN SSSR, M., 1962.

[8] L. H. Jones, J. Chem. Phys. **22**, 217 (1954).

[9] W. R. Busing, J. Chem. Phys. **23**, 933 (1955).

[10] R. G. Snyder, J. Kumamoto, and J. A. Ibers, J. Chem. Phys. **33**, 1171 (1960).

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